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Improvement of Polypropylene Nonwoven Fabric Antibacterial Properties by the Direct Fluorination

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An one-step "dry" method of the direct fluorination was applied to highly improve antibacterial properties of polypropylene nonwoven fabric. A treatment of polypropylene nonwoven fabric with F2/N2 mixture highly improved the barrier antibacterial properties with respect to test bacteria – Gram-positive Staphylococcus aurous (total reproduction suppression) and partially for Gram-negative Escherichia coli. A treatment with F2/N2/O2 mixture totally suppressed Candida albicans microfungus reproduction. Polypropylene nonwoven fabric tensile strength was slightly increased after fluorination.

Introduction.

Polypropylene nonwoven fabric (PPNWF) is extensively used in house and roads building, agriculture, sewing industry, medicine, as filtering materials etc. The most important PPNWF application is a fabrication of disposable hospital clothes and bed linen with the aim to improve staff and patients infection resistance against various pathogens (gram-positive, gram-negative, microfungus). Disposable clothes fabricated from PPNWF is sterilized after fabrication. Its antimicrobial properties are improved after treatment with specific antimicrobial agents but the low adhesion of such agents to the clothes fibres does not provide long lasting antimicrobial effect. We propose an alternative approach to greatly improve PPNWF barrier antimicrobial properties: chemical one-step covalent modification of the PPNWF by the direct fluorination. The direct fluorination of polymers is a heterogeneous reaction of gaseous fluorine mixtures with a polymer surface[1-7]. Upon the fluorination of the aliphatic polymers hydrogen atoms are replaced with fluorine atoms to convert hydrocarbons to totally or partially fluorinated polymers. The fluorination degree and chemical composition of the upper surface layer depends on a polymer nature and treatment conditions (fluorinating mixture composition and pressure, treatment duration etc.). Some crosslinking, destruction and oxygenation also may take place. Formed -FC=O groups hydrolysis by an atmospheric moisture is followed by COOH groups formation. The direct fluorination of polymers proceeds spontaneously even at room temperature and does not need any initiation. Previously it was shown that the polymers treated with fluorine consist of a fluorinated polymer layer and an untreated one which are separated by a very thin (<<100 nm thick) transient layer[2-5, 8]. In this work we are reporting for the first time the direct fluorination of PPNWF with the F_2-O_2-N_2 mixture. The characterization of the fluorinated material has shown that it acquired barrier antimicrobial properties.

Results.

Multiple Attenuated Total Reflection (MATR) FTIR spectra of PPNWF are shown in the figure 1. The main feature of the fluorinated PPNWF spectra is an origin of a very broad diffuse band over 950-1300 cm^{-1} which is due to an overlapping of C-Fx groups absorption (x=1, 2 and 3)[2-5, 9]. The intensities of all the CH_3, CH_2 and CH bands over 3000-2800 and 1500-800 cm^{-1} range were also markedly decreased. A weak band at 1730-1750 cm^{-1} is due to the –COOH band which was originated due to a hydrolysis of -COF band: -COF + $H_2O \rightarrow$ -COOH + HF[2-5]. The fluorinated layer thickness δ_F=0.32±0.03 μm was estimated as described in [2-5, 8, 10] and was much less than

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the depth of the IR probe light penetration inside a polymer. Therefore the FTIR spectrum of the fluorinated PPNWF consists of overlapping spectra of both fluorinated and pristine layers of the polymer. Nevertheless it is possible to qualitatively estimate the relative fluorination degree of different CH_x groups by a change of the appropriate bands area: CH_3 (1378 cm^{-1}), CH_2 (1438 cm^{-1}) and CH (1362 cm^{-1}). For the case of treatment with F_2/N_2 mixture the percentage of nonfluorinated groups can be estimated as 28.6%, 23.0% and 36.2% for the groups CH_3, CH_2 and CH respectively. For the case of a treatment with $F_2/O_2/N_2$ mixture the percentage of nonfluorinated groups can be estimated as 44.7%, 35.0% and 58.7% for the groups CH_3, CH_2 and CH respectively. It means that the reactivity of the different groups is decreased in the CH_2-CH_3-CH sequence. The FTIR data confirmed that the fluorinated layer thickness is smaller for the case of treatment with $F_2/O_2/N_2$ mixture as compared with F_2/N_2 mixture treatment in accordance with [10].

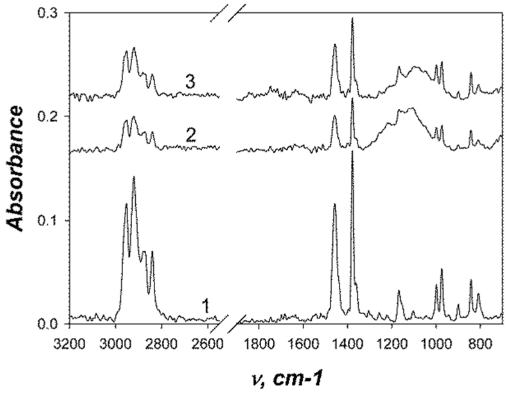
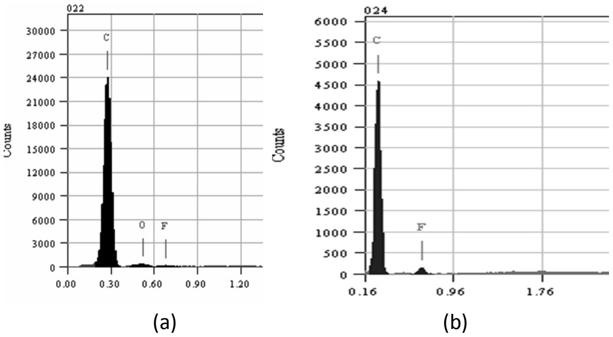


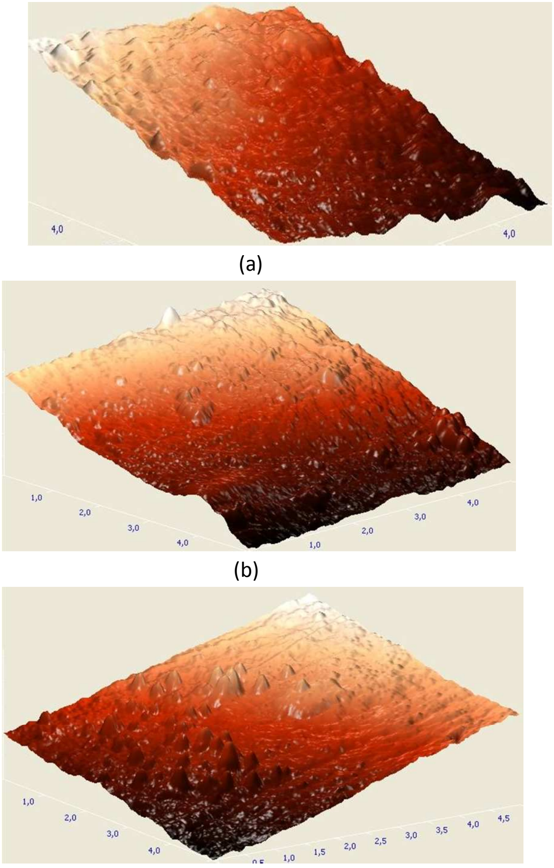
Fig.1. MATR FTIR spectra of PPNWF: untreated (1), treated with $10\%F_2+90\%N_2$ mixture during 30 min (2) and treated with $9\%F_2+9\%O_2+82\%N_2$ mixture during 30 min (3).

The chemical composition of the PPNWF top layer was studied by an energy-dispersive X-ray spectroscopy (EDX) (fig.2). For the case of PPNWF treated with $9\%F_2+9\%O_2+82\%N_2$ mixture the surface composition was as follows: C – 94.3±0.1%, O - 4.5±0.9%, F – 1.2±0.4%. For the case of a treatment with $10\%F_2+90\%N_2$ mixture the composition was as follows: C – 94.7±0.1%, F – 5.3±0.4%. According to the previous research results[2-5, 8, 10] the thickness of the fluorinated layer can be estimated as 0.32±0.03 μm for the case of a treatment with $10\%F_2+90\%N_2$ mixture and less than 0.06 μm for the case of a treatment with $9\%F_2+9\%O_2+82\%N_2$ mixture. The penetration depth of electrons in EDX measurements is close to 1.5 μm therefore the EDX data indicated the chemical composition of the fluorinated layer and the pristine (not fluorinated) polymer layers together. Very tentatively a real concentration of fluorine in the fluorinated layer can be estimated as 25-27%. For the case of a treatment with $9\%F_2+9\%O_2+82\%N_2$ mixture the fluorine concentration is much less – around 6%. The surface fluorinated layer is also highly oxidized – an oxygen concentration can be estimated as 20-25%.



(a) (b)

Fig.2. EDX spectra of PPNWF treated during 30 min with $9\%F_2+9\%O_2+82\%N_2$ mixture (a) and with $10\%F_2+90\%N_2$ mixture (b).



(a)

(b)

(c)

Fig.3. AFM pictures 5x5 μm in area. Pristine PP film (a), treated with $10\%F_2+90\%N_2$ mixture (b) and treated with $9\%F_2+9\%O_2+82\%N_2$ mixture (c).

PPNWF surface should be made more hydrophobic for easier blood and other organic pollutions removal from disposable robes and linen. Polymers hydrophobicity depends on two factors – a chemical composition and a surface texture[11]. High hydrophobicity is possible only with a high PPNWF surface roughness. In AFM experiments we have shown that the direct fluorination resulted in a marked increase of the surface roughness in accordance with [12-13] (fig.3). We have studied not PPNWF but flat PP films because an application of AFM to PP nonwoven fabric is highly complicated (obstructed) by technology reasons. Therefore we considered a flat PP film as a model object quite similar to PP fibers in PPNWF. The average roughness of a pristine PP film is 3.3 nm. After treatment with $F_2/O_2/N_2$ mixture an average roughness of PP film is 5.6 nm, after treatment with F_2/N_2 mixture – 6.6 nm. A mean-square roughness was equal to 1.4, 2.7 and 2.5 nm for the case of pristine PPNWF, treated with $F_2/O_2/N_2$ and with F_2/N_2 mixture respectively. Therefore the direct fluorination simultaneously and markedly changes the polymer materials surface roughness and its chemical composition.

PP films treatment with $F_2/O_2/N_2$ mixture resulted in a small decrease of the water contact angle (from 77±1 for the pristine film to 64±1 degrees for the fluorinated one, i.e. the hydrophilicity was improved), a treatment with F_2/N_2 mixture resulted in a water contact angle small increase (from 77±1 to 86±2 degrees, i.e. the hydrophobicity was improved). In the first case C=O-containing groups with a high surface energy were formed, in the second case - fluorinated groups with a low surface energy which is in a good agreement with the FTIR spectra of the treated PPNWF (Fig.1). It seems that the prevailing influence of the direct fluorination on the contact angle of PP films is mainly due to a change of the chemical composition but not due to a roughness increase.

The fluorinated PPNWF water contact angle is higher than that of the PP films fluorinated under the same conditions. A treatment of PPNWF resulted in a small increase (+6…8 degrees, i.e. the hydrophobicity was improved) for the case of a treatment with F_2/N_2 mixtures during 10 and 30 minutes. Changes in the chemical composition are identical. Therefore, the roughness of the fluorinated PPNWF has a greater influence on the hydrophobicity than the roughness of the PP fluorinated film. This is due to a complex fibrous structure of a nonwoven material which provides a multi-modal texture necessary for the realization of the heterogeneous wetting mechanism. Hence PPNWF hydrophobicity can be slightly improved.

The fluorination of the polymer surface may improve its resistance to microfungi as it was observed in [14-15]. Thus we can suggest that the fluorinated PPNWF acquires the ability to inactivate pathogenic bacteria and microfungi in contact with them, that is a barrier antimicrobial property. Generally speaking, both non-migrating covalently attached fluorine and unbound products of -COF hydrolysis can contribute to the barrier antimicrobial properties of the fluorinated fabric. Therefore two different methods[16-17] were applied to characterize the fluorination influence on the PPNWF barrier antimicrobial properties with the respect to the mobility of the antimicrobial species.

Both methods can be considered as quantitative. The first applied method indicated that microbes-free area was not formed around the sample. It means that this method cannot be applied for our samples because that method was developed especially for the antibacterial substances which are not covalently bonded with the substrate and can migrate to the solution.

When the fluorinated PPNWF was placed onto the nutrient medium (agar) with inculcated test microbes (*Staphylococcus aureus, Escherichia coli, Candida albicans*) we have not observed a microbes-free area formation around the sample (method number 1). That indicates that the fluorinated groups on the surface of PPNWF are not substantially hydrolyzed and do not diffuse into the solution. Therefore we have used another method for the measurements of the growth inhibition. To study pathogenic microorganism growth inhibition a fluorinated PPNWF was placed in a saline solution contained appropriate microbes. For comparison we have used the pristine material. For the case of pristine materials the amount of grown colonies was taken as 100%. The test results are shown in the Table 1. The data of three measurements were averaged for each sample. The standard deviation was calculated to be from 10 to 12% for all the tested samples. The measurements were carried out for (i) the freshly fluorinated, (ii) washed in water (just after washing) and (iii) for washed samples stored during 5 months in air. The data of the biocidal (antimicrobial) effect for each sample coincided within 10-12% accuracy. Therefore we can conclude that the fluorine was covalently bonded with a polypropylene surface and also a washing and long storage duration does not influence the PPNWF antimicrobial properties.

Table 1. Influence of treatment conditions on the barrier antimicrobial properties of PPNWF according to ASTM E 2149.

Fluorinating mixture and treatment duration	Bacteria & microfungus amount increase (%) / antimicrobial effect		
	Bacteria		Microfungus
	Escherichia coli	*Staphylococcus aureus*	*Candida albicans*
Pristine PPNWF	100 / absence of antimicrobial effect		
$9\%F_2+9\%O_2+82\%N_2$, 30 min.	14 / low antimicrobial effect	56 / absence of antimicrobial effect	0 / excellent antimicrobial effect
$10\%F_2+90\%N_2$ 30 min.	6 / good antimicrobial effect	0 / excellent antimicrobial effect	59 / absence of antimicrobial effect

For the case of treatment with F_2/N_2 mixture excellent antimicrobial effect was obtained for *Staphylococcus aureus* and good antimicrobial effect - for *Escherichia coli* microbes. A treatment with $F_2/O_2/N_2$ mixture suppresses mainly microfungus. It means that the direct fluorination exhibits a selective antimicrobial effect depending on the fluorination conditions. From the above data it can be concluded that an antimicrobial effect is probably determined by the presence of CF_3, CF_2- and CHF groups on the polymer surface for the case of Gram-positive and Gram-negative bacteria and COF, COOH groups for the case of microfungus.

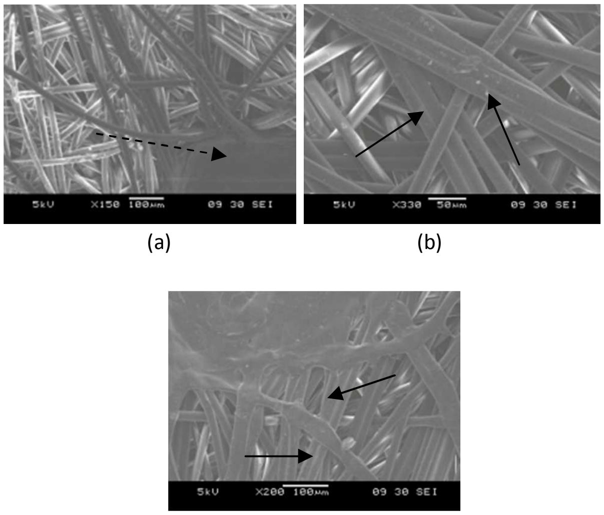
The influence of the direct fluorination on the tensile strength and elongation at break are collected in the Table 2. 10 to 14 measurements data were averaged for each sample. Mechanical properties of PP films were slightly worsened for the case of fluorination: tensile strength was decreased by 7-15%, elongation at break was decreased also. The reason of such a decrease might be due to a destruction of polymer chains. The tensile strength of PP yarns was slightly decreased (by 1-3%) under the fluorination but the elongation at break remains constant within the measurements accuracy.

The direct fluorination of the PPNWF with $F_2/O_2/N_2$ mixtures resulted in a marked tensile strength increase (up to +24% for a treatment duration 10 and 30 min.) in longitudinal direction and no change across the width direction. A treatment with F_2/N_2 mixture did not influence (within the measurements accuracy) the tensile strength in both longitudinal and width directions.

Table 2. The fluorination conditions influence on PP films, complex yarns and nonwoven fabric tensile strength and elongation at break.

Fluorinating mixture and treatment duration	Tensile strength, N	Elongation at break, %
PP films 30 μm in thickness		
No treatment	540 ± 45	308 ± 51
9%F_2+9%O_2+82%N_2 mixture, 30 min.	503 ± 57	225 ± 35
10%F_2+90%N_2 mixture, 30 min.	469 ± 83	212 ± 55
PP complex yarns 55 μm in diameter, consisting of 140 filaments-fibers		
No treatment	592 ± 4	56 ± 3
9%F_2+9%O_2+82%N_2 mixture, 30 min.	586 ± 4	52 ± 3
10%F_2+90%N_2 mixture, 30 min.	577 ± 5	58 ± 3
PPNWF *with surface density 40 g/cm^3 in longitudinal direction*		
No treatment	55.2 ± 5.7	40 ± 6
9%F_2+9%O_2+82%N_2 mixture, 3 min.	60.3 ± 4.3	34 ± 6
9%F_2+9%O_2+82%N_2 mixture, 10 min.	68.5 ± 6.7	38 ± 5
9%F_2+9%O_2+82%N_2 mixture, 30 min.	68.5 ± 6.7	37 ± 5
10%F_2+90%N_2 mixture, 3 min.	54.3 ± 2.9	23 ± 8
10%F_2+90%N_2 mixture, 10 min.	57.1 ± 4.5	31 ± 4
10%F_2+90%N_2 mixture, 30 min.	59.2 ± 4.5	32 ± 4
PPNWF *across width direction*		
No treatment	39.4 ± 1.8	46 ± 7
9%F_2+9%O_2+82%N_2 mixture, 3 min.	39.1 ±4.1	47 ± 9
9%F_2+9%O_2+82%N_2 mixture, 10 min.	40.9 ± 4.0	38 ± 5
9%F_2+9%O_2+82%N_2 mixture, 30 min.	42.1 ± 1.4	36 ± 4
10%F_2+90%N_2 mixture, 3 min.	39.7 ± 5.0	39 ± 4
10%F_2+90%N_2 mixture, 10 min.	41.6 ± 4.9	38 ± 4
10%F_2+90%N_2 mixture, 30 min.	42.3 ± 1.3	36 ± 4

SEM microscopy indicated that the direct fluorination resulted in a "welding" of neighboring yarns (welding places are indicated by arrows in the fig.4). Welding might occur due to a great energy release during the fluorination process (highly exothermic one) and a partial melting of the fiber surface because the heat transfer from fibers to environment (gaseous atmosphere) and fiber cooling is highly limited. As a result, the surface layer of the PPNWF became more perfect and structural defects were eliminated and the tensile strength could be improved.



(a) (b)

(c)

Fig.4. SEM pictures of the pristine PPNWF (a), treated with 9%F_2+9%O_2+82%N_2 mixture (b) and with 10%F_2+90%N_2 mixture (c). A large spot in the pristine PPNWF SEM picture (a) indicates the place where material was pierced by heated needle during fabrication (dashed arrow). Welded due to the fluorination places are indicated by arrows (b, c).

Experimental section.

The direct fluorination was carried out in static conditions in closed vessels at a room temperature (20±2°C). The fluorination equipment was fabricated from low-carbon steel, stainless steel and Teflon®. The polymer sample was placed inside a vessel, evacuated to residual vapor pressure <1 Pa and a vessel was filled with a fluorinating mixture. The fluorine consumption was always less than 20% during the fluorination. An amount of impurities in F_2 and O_2 was less than 0.1 and 0.01 volume % respectively. Fluorine is a toxic gas so strong precautions must be taken when using fluorine. All the details of experimental vacuum equipment (reaction vessels, connectors, vacuum valves, pipes, gaskets etc.) which contact with fluorine must be fabricated from steel, stainless steel and Teflon. Not consumed fluorine and the reaction product HF must be neutralized by passing through a special trap filled with crushed marble (or zeolite) and sodium fluoride (NaF). The working place must be equipped with reliable vent system. The vacuum pump outlet must be connected to the vent system. The personnel must be supplied with gas masks for the case of any incident. PPNWFs with a surface density 40 and 80 g/cm^3 were purchased from "Shchekino Khimvolokno Ltd)" (city Shchekino, Russia). PP yarn 55 µm in diameter, consisting of 140 filaments was obtained from the melt on a laboratory plant. PP films 30 μm in thickness were purchased from "Pack-Trade Ltd" (city Ivanovo, Russia). The polymer surface texture and chemical composition was studied by a scanning electron microscope JSM 6380LA ("JEOL") and atomic force microscope P 47-PRO NT-MDT ("Solver", Russia). FTIR spectra were measured by FTIR spectrometer FT-02 ("Lumex Ltd", Russia) equipped with a MATR ZnSe accessory (45^{o}) at 4 cm^{-1} resolution. Water contact angles were measured by a conventional Owens-Wendt method[18]. The tensile strength and elongation at break were measured by testing machine 2099-P-5 ("Tochpribor", Russia) according to GOST 6611.2-73 (ISO 2062-72, ISO 6939-88). Fibers length was equal to 250 mm, the stretching speed used was equal to 300 mm/min. PPNWF was tested according to GOST P 53226-2008 (ISO 9073, ISO 10319). PPNWF samples 200 mm in length and 50 mm in width were tested at the stretching speed 300 mm/min. PPNWF antibacterial properties were studied for typical test cultures: Staphylococcus aureus (gram-positive), Escherichia coli strain M-17 (gram-negative) and Candida albicans (microfungus). Two methods were used to evaluate antimicrobial properties. The first method was based on the measurement of microbe suppression zone around the tested sample[16]. The sample was placed in the Petri dish onto nutrient medium (agar) with test–microbes inculcated and the microbes-free area size around the sample was measured. This method is traditionally used to study antimicrobial efficiency of the samples where an active substance diffuses from the fiber into a liquid phase. The second method can be considered as a modified microbiological test ASTM E2149 when a chopped PPNWF was placed in a physiological solution contained appropriate microbes[17]. In 24 hours an amount of grown microbe's colonies has been counted. To avoid counting mistakes and reduce the testing duration the amount of grown colonies was measured by a change in the turbidity of the solution (a nephelometry method). For pristine materials the grown colonies amount was taken as 100%. This method is used to test antimicrobial substances which are chemically bonded to the fibers and do not migrate into the solution. The amount of grown colonies more than 10% was assumed as insufficient microbe suppression, 10 to 1% – as good and less than 1% – excellent one.

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Conclusions.

The direct fluorination of the PPNWF resulted in a remarkable improvement of its barrier antimicrobial properties which are defined mainly by the fluorinating mixture composition. A treatment with F_2/N_2 mixture resulted in both Gram-positive and Gram-negative bacteria suppression. $F_2/O_2/N_2$ mixture is more effective in a case of pathogenic microfungus (their reproduction was totally suppressed). A treatment with F_2/N_2 mixture resulted also in a slight hydrophobicity improvement. The direct fluorination resulted in a remarkable improvement of the PPNWF tensile strength in longitudinal direction and practically did not influence PPNWF mechanical properties in the width direction. On the base of the above data we can conclude that the direct fluorination can markedly improve the PPNWF barrier antimicrobial properties without loss (or even with some improvement) of its tensile strength.

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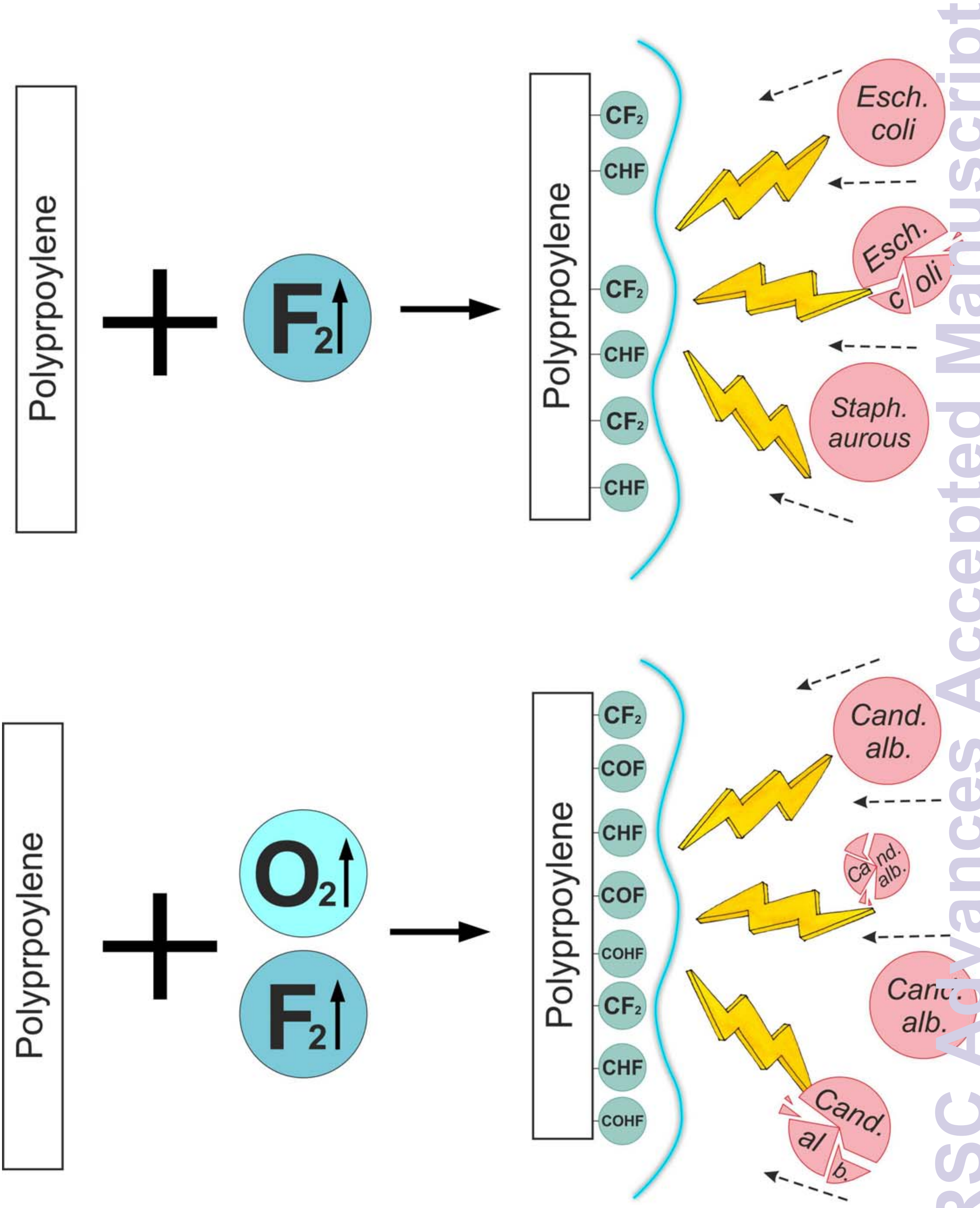
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